

Introduction to Nanoscience

Study Guide

Chapter 8 - Introduction

This chapter is an optional chapter but one that should be, at the least, discussed in at least one daily lecture. It addresses the thermodynamics of nanosystems, including that of living things, and brings up several interesting aspects of thermodynamics and their applicability to nanosystems.

Much of the chapter relates to nanothermodynamics via verbal dialogue and discusses the need for a fourth law of thermodynamics— quite a revolutionary request! Some of the chapter shows the basic equations of thermodynamics and projects modified versions onto nanomaterials.

Nanothermodynamics is theoretically a new area of thermodynamics— a thermodynamics that is supposedly describes the behavior of nanomaterials better than does traditional thermodynamics.

Chapter Objectives:

- Review the meaning of extensive properties
- Review the meaning of intensive properties
- Review the meaning of state functions
- Acquire a deep understanding of entropy and its consequences
- Read all material presented about living systems and thermodynamics
- Review the meaning of the system, its surroundings and equilibrium ($\Delta G = 0$)
- Review the fundamental four laws of thermodynamics: Zeroeth, First, Second and Third
- When studying nanomaterials, keep in mind the 4 laws of thermodynamics
- Understand why a fourth law of thermodynamics may be required to explain the behavior of nanomaterials and living systems
- Review the fundamental equations of thermodynamics. It helps put a perspective on what is to follow.
- Equilibrium constants and reaction kinetics are briefly reviewed

- Acquire a basic feel for the significance of statistical mechanics, microstates and macrostates
- Understand Boltzmann's equation and its relevance to thermodynamics:

$$S = k_B \ln W$$
- Know the other kinds of thermodynamics: near-equilibrium thermodynamics, non-equilibrium thermodynamics, non-linear thermodynamics, steady-state systems and pseudo-equilibrium thermodynamics. And don't forget quasi-equilibrium thermodynamics.
- Do not be too concerned with the Onsager relations... they were presented to show that a link with a "fourth law of thermodynamics" is not a new concept brought about by the onset of nanotechnology.
- Understand the meaning a "dissipative process".
- Delve into the thermodynamics of cellular and subcellular systems beyond the scope of this text
- Delve into the meaning of "rectifying behavior" of kinesin and RNA polymerase
- Look into why thermal fluctuations may have significant effects on small systems
- Familiarize yourself with the thermodynamics of Terrell Hill and how he stated that the thermodynamics of small systems will usually be different in different environments.
- We recommend that you read the paper referencing the transfer of random heat to latex beads (please see text)
- Decide for yourself the validity of classical thermodynamics as applied to nanosystems
- Review the growth dynamics of single-walled nanotubes
- Nonextensivity and nonintensity are new concepts to thermodynamics. Review their meaning

The discussions in this text are limited to qualitative treatment without the support of detailed quantitative material. Obviously there is not much available space in an introductory text to do so.

The Energy Continuum Importantly, thermodynamics is centered on the energy continuum— the smooth (or dramatic) flow of energy from one system to another. No matter how large or small, energy is conserved according to the First Law of

Thermodynamics. Even with regard to nanosystems and biological systems, there is never a conversation focused on the need to redefine the 1st Law.

Living Things Note also that the concept of equilibrium when applied to living things is equivalent to a death warrant. Cellular equilibrium is the same thing as cellular death. This does not preclude that equilibria exist in cells; they most certainly do. Cellular systems are better defined as ones in a steady-state equilibrium; one of constant motion, exchange and function. However, once the power supply is turned off, then it all stops.

The implication in the text that living things follow a more kinetically oriented character rather than one that is more purely thermodynamic is indeed an interesting proposition.

Discussion Topic: Please discuss with your classmates and others about the thermodynamics of living things. Kinetic or thermodynamic? Equilibrium or steady-state? and why nanomaterials are fundamental to life?

Extensive and Intensive Properties Every textbook on thermodynamics introduces the terms extensive and intensive. Our text does offer more detail about these terms and their fundamental importance to thermodynamics. We define EVERYTHING through them. They are the pillars of our current thermodynamic understanding.

One of the tenets of nanothermodynamics is that non-extensivity and non-intensivity are the rule rather than the exception. How so? What exactly are non-extensivity and non-intensivity?

We understand that nanomaterials are affected more by their immediate environment. In other words, a quantum dot may change its very structure under the right conditions of temperature and pressure or chemical environment. Intensive properties then do not hold for this nanomaterial. With nanomaterials, how far to we go to define the system? If we consider that our system is the entire universe, then we do not, most likely, require a 4th Law of Thermodynamics to explain things. However if we consider a system to be the confined space within the pore channel of an anodically-formed alumina, then we have not only different thermodynamics (perhaps) but most certainly different chemistry.

Laws of Thermodynamics We shall make no attempt to further our discussion about these laws. Please refer to any number of excellent references in your library. The same is in effect for the fundamental equations of thermodynamics and the expressions used in defining equilibrium and kinetics. Add statistical mechanics to this list.

Other Kinds of Thermodynamics? Are there other kinds of thermodynamics or do we just conveniently draw boundaries around things we are not so certain. Most non-equilibrium thermodynamic studies revolve around or near equilibrium. Thermodynamics, like anything else, lives in a continuum. We are able to lift from that continuum what apparently seem to be different kinds of thermodynamics.

At the nanoscale, it seems obvious that very small materials, due to inherent metastability, are able to alter shape, form and structure due to interaction with the immediate environment. One of the keys is the concept of reversibility. Are nanomaterials more prone to reversibility?

Discussion Topic: Discuss the various forms of thermodynamics and find common links.

Understanding nanothermodynamics in *cellular systems* is indeed a challenging area. Kinesin, for example, moves large objects relative to its size in cells. That action requires an input of energy. According to the latest research, kinesin, unlike its macroscopic steady-state devices, is able to harvest thermal fluctuations from the surrounding cellular medium to help power its motion in addition to the ATP-power— and this motion only occurs in one direction, a process called energy rectification. The key point: thermal fluctuations are not significant at the macroscale.

A synthetic system was also applied to study fluctuations and the ability of a small system to utilize energy from that source. Latex beads moved by IR-laser tweezers were shown to exhibit negative entropy over short time frames— clearly a violation of the 2nd Law of Thermodynamics. We mentioned a while back that the timescale for nanosystems was on the whole much faster than it is for macrosystems. These moments of negentropy occurred only for short time frames. When the experiment was measured over longer time frames, entropy behaved properly. In other words, nanoscale systems can become more ordered over very short time frames.

SWNT Growth The thermodynamic parameters of SWNT growth has been modeled with the application of classical thermodynamics. For example, it was possible to calculate the relative heat of formation without consideration of nanoscale phenomena. This was also the case with estimates of fullerene heats of formation by the process of calorimetry. In both cases, bulk amounts of SWNT or fullerene were used in the studies.

Small System Thermodynamics began with T.L. Hill. In his treatment, Hill simply added a term to Gibbs equations that accounted for small particles. This kind of treatment is accomplished all the time in thermodynamics. For example, if we are concerned with small particle nucleation, we need to simply add on a term that includes surface effects in the treatment.

Chemical potential as defined by Willard Gibbs himself is

"If to any homogeneous mass in a state of hydrostatic stress we suppose an infinitesimal quantity of any substance to be added, the mass remaining homogeneous and its entropy and volume remaining unchanged, the increase of the energy of the mass divided by the quantity of the substance added is the potential for that substance in the mass considered."

Defined as $G = \mu N$ where it is usually represented as $(\partial G/\partial n)_{TP} = \mu$. If other factors need to be considered, one just adds them on. So essentially, what Hill is saying that all is well with the thermodynamic treatment of free energy for small systems if a subdivision potential is tacked on to the expression. That expression takes the form of $G = \bar{\mu}N$. This last term disappears as the system gets larger and larger.

Non-intensivity and non-extensivity go hand in hand with systems that are considered to be nonergodic. This topic is not easy to visualize and we will not spend much time on it (within the context of this text), but A.K. Rajagopal summarizes it quite adequately. Their goal was to derive a consistent description of nanosystems from first principles. Classical thermodynamics is based on the four Gibbsian potentials (U, H, A and G) from which the four Maxwell relations and the Gibbs-Duhem relation were derived. However, the jump from them into nanometric systems just did not compute.

Both equilibrium and non-equilibrium thermodynamics came into question according to Rajagopal. The two approaches to address the dichotomy consisted of the Hill approach discussed previously in which surface effects are taken into consideration and the other modified the additive properties into pseudo-additive properties (but consistent with the zeroeth law of thermodynamics).

Suffice for now to understand that there may be a difference (we say may because the field is so new and some believe it is simply a matter of statistical fluctuations) between classical thermodynamics and the thermodynamics of small systems.

Chapter Summary

- A chapter such as this is beyond the scope of the text and was presented solely to introduce the subject and add some material to the arsenal of differences between macro and nano systems.
- Nanosystems are affected by their immediate environment. Macrosystems not so much
- What exactly is non-extensivity? It is non-additivity, a concept anathema to traditional equilibrium thermodynamics.
- What is non-intensivity? Intensive properties change in nanomaterials.... properties like density, for example, can change depending on the environment.

